

Phase separation and the possibility of orbital liquid states in CMR manganites. A ^{139}La NMR study.

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^{139}La NMR spin-lattice relaxation rate $1/T_1$ and rf enhancement experiments provide evidence that the low temperature regime of the ferromagnetic (FM) phase of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ segregates into highly-conductive and poorly-conductive FM regions, associated with differences in the orbital structure. Remarkably, phase separation is accompanied with the appearance of an extra NMR signal from FM regions with vanishingly small magnetic anisotropy. This feature has been attributed to the appearance of regions with strong orbital fluctuations, resembling droplets of an orbital liquid within the inhomogeneous FM matrix.

The origin of the electronic properties of mixed valence manganites with the general formula $\text{R}_{1-x}\text{D}_x\text{MnO}_3$ ($\text{R}=\text{rare earth}$, $\text{D}=\text{Ca, Ba, Sr}$), poses one of the most exciting open problems in the physics of strongly correlated electron systems. Initially, these properties were determined in the framework of the double exchange (DE) model [1], which is based on the strong Hund's coupling between hopping e_g and underlying t_{2g} electrons in successive $\text{Mn}^{4+,3+}$ sites. However, in the last years experiments have shown that DE is inadequate for the full description of the complex properties of these systems. For example, in the low doping regime an important question concerns the origin of the ferromagnetic insulating (FMI) to ferromagnetic conductive (FMC) phase transition, which at first sight appears to contradict the DE model. Recent x -ray resonant scattering [2] and NMR [3] experiments have shown that this transition is controlled rather by orbital than by spin degrees of freedom. Another question concerns the nature of the mixed FMI-FMC phase, which has been observed close to the corresponding phase boundary [3]. According to theoretical models including orbital ordering (OO) and Jahn-Teller distortions, such phase coexistence might indicate the presence of electronic phase separation [4], [5]. However, it is still experimentally unclear whether the observed mixed phases possess the same intrinsic electronic properties as the constituting pure phases, or whether they form microscopically a "third" novel electronic state.

In this letter, we demonstrate experimentally for the first time that phase separation, occurring in the low temperature regime of FM La based manganites, is accompanied with a significant change of the e_g electron mobility at a local level. Specifically, we show that by cooling the high temperature "homogeneous" FMC phase breaks into FMC and FMI regions with enhanced - respectively

reduced - electron mobility in respect to the high temperature phase. Most important, the formation of the mixed phase is accompanied with the detection of FM regions with extremely low magnetic anisotropy, which is explained as showing the formation of regions with strong orbital fluctuations.

In order to label the various magnetic structures according to their electronic transport properties and OO we have employed ^{139}La spin lattice relaxation, and ^{139}La radiofrequency (rf) enhancement experiments. Particularly, we have shown that the abrupt decrease of the ^{139}La NMR spin-lattice relaxation rate ($1/T_1$) in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ by decreasing temperature or increasing x , provides a direct measure of delocalization of the e_g electrons. On the other hand, rf enhancement experiments may be used in order to monitor subtle changes of the magnetic anisotropy at a local level. In such experiments the NMR signal intensity I is recorded as a function of the intensity H_1 or the duration τ of the applied rf field [6]. The obtained curves follow an asymmetric bell-shaped law with maximum at $n\gamma H_1\tau = 2\pi/3$, which allows the calculation of the rf enhancement factor n [7]. Considering that the rf enhancement reflects the coherent response of the electron magnetic moments to an external rf field, it is clear that any variation of the magnetic anisotropy field H_A will be directly reflected on n [8].

Experiments were performed on polycrystalline samples prepared by annealing stoichiometric amounts of the corresponding oxides in air at 1300 to 1400 $^\circ\text{C}$. All samples were then characterized structurally at room temperature with a D500 Siemens x -ray diffractometer, and magnetically with a SQUID magnetometer. The obtained crystallographic and magnetic data were found to be in accordance with literature. ^{139}La NMR spectra

in zero external magnetic field were acquired by applying a two pulse spin-echo technique, with pulse widths $t_{p1} = t_{p2} = 0.6 \mu\text{sec}$ at very low rf power level, due to the very strong rf enhancement that characterizes FM materials [7]. The obtained ^{139}La spectra consist of broad lines located at $\simeq 20 \text{ MHz}$, which unambiguously are attributed to FM regions with fully polarized Mn spin octants [9], [10], [11]. T_1 was then measured at the peak of the spectra, by applying a saturation recovery technique and fit with a multiexponential recovery law as in previous works [12].

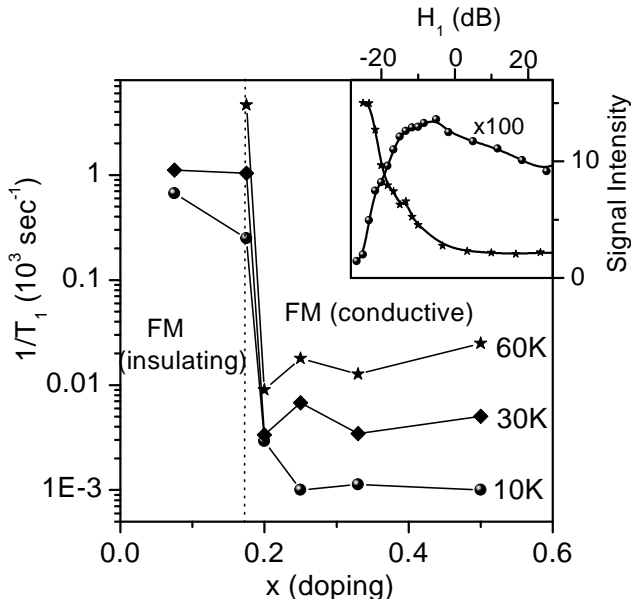


FIG. 1. ^{139}La $1/T_1$ of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, as a function of x . The inset demonstrates the ^{139}La NMR signal intensity as a function of the rf field H_1 for $x = 0.1$ (●) and 0.33 (★). All spin lattice relaxation experiments were performed at $H_1 = -10\text{dB} \simeq 3\text{Gauss}$.

Figure 1, exhibits ^{139}La $1/T_1$ vs. x measurements of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ at three different temperatures. It is observed that by increasing x , $1/T_1$ decreases abruptly by almost two orders of magnitude, at $x \approx 0.175$, which according to the literature defines the phase boundary between the FMI and FMC regimes of the $T-x$ phase diagram. This is a remarkable result, which shows that e_g electrons play a major role in ^{139}La spin-lattice relaxation phenomena. In order to describe qualitatively this behaviour, we have used the general approach invented by Warren for relaxation studies of metal-insulator transitions in liquid semiconductors [13]. In general, nuclear spin-lattice relaxation in CMR manganites is determined by fluctuations of the local magnetic field H_{loc} at the nuclear sites, (i) due to e_g electron hopping, and (ii) due to interaction with spin waves. However, in systems with spin-polarized conduction bands, like CMR manganites [14], spin wave scattering is determined by weak two-magnon processes, and ^{139}La $1/T_1$ should be dominated by direct e_g electron spin flips, if energetically allowed.

The latter assumption is supported by recent tight binding calculations in FM CMR manganites [15], which show that in the presence of electron-phonon coupling the minority $t_{2g}(\downarrow)$ band attains a small finite DOS at E_F , and spin flip between $e_g(\uparrow)$ and $t_{2g}(\downarrow)$ energy states is in principle possible. Following Warren's approximation, and by assuming an exponentially decaying autocorrelation function for the fluctuations of H_{loc} , we may easily arrive at the expression [13] $1/T_1 \simeq TN(E_F)^2\tau_e/\{\hbar N(E_F)\}$, where τ_e has the significance of the lifetime residence of e_g electrons on the Mn sites.

In case of delocalised electron states, where the electron mean-free path $\ell \gg a$ (a is the distance to the nearest neighbour), $\tau_e = a/v_F = \hbar N(E_F)$ [13], and the above relation transforms to the standard Korringa relation, $1/T_1 \propto TN^2(E_F)$. However, in case of charge localization, i.e. for $\tau_e \gg \hbar N(E_F)$, $1/T_1$ is sufficiently higher than for delocalised electron states. Evidently, the abrupt reduction of $1/T_1$ in Figure 1 provides a direct evidence of conductivity enhancement, due to delocalization of the e_g electron states. Such a behaviour is reminiscence of a sharp metal-insulator transition of the Anderson type, and not of a percolative transition as proposed by many authors. Most notably, the onset of metallicity for $x \geq 0.175$ is characterized by a strong amplification of the rf enhancement factor, as recently reported by Dho et al. [16]. This is clearly observed in the inset of Figure 1, which exhibits ^{139}La NMR I vs. H_1 curves of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $x = 0.1$, and 0.33 , at $T = 5\text{K}$. For $x = 0.33$ the maximum of the I vs. H_1 curve shifts to extremely low H_1 values, which indicates a considerable reduction of the magnetic anisotropy [8]. Considering that (i) H_A is mainly determined by the LS coupling, and (ii) according to previous works on Sr-doped systems [2] the metal-insulator transition correlates with OO changes, we argue that the observed change in the rf enhancement reflects a substantial modification in the orbital structure.

Figure 2 demonstrates ^{139}La $1/T_1$ vs. T measurements for $x = 0.25$. It is observed that by decreasing temperature $1/T_1$ decreases almost exponentially, in agreement with previous works in relevant materials [17]. For $T < 30\text{K}$ $1/T_1$ exhibits an almost stepwise decrease, which may be assigned to enhancement of the e_g electron hopping below that temperature. Remarkably, the steep descent of $1/T_1$ is accompanied with the appearance of ^{55}Mn NMR signal from FMI regions, as shown in ref. [3]. Such FMI regions can not be detected by ^{139}La NMR for $x \geq 0.175$, because signals from FMI regions with extremely low T_1 s are masked from the much stronger signals from FMC regions. Apparently, the overall resistivity enhancement below 30K (inset of Figure 2) may be attributed to restriction of the conductivity channels below that temperature. These results demonstrate that for $T \leq 30\text{K}$ the system splits into regions with enhanced - respectively reduced - conductivity in comparison to the high temperature FMC phase.

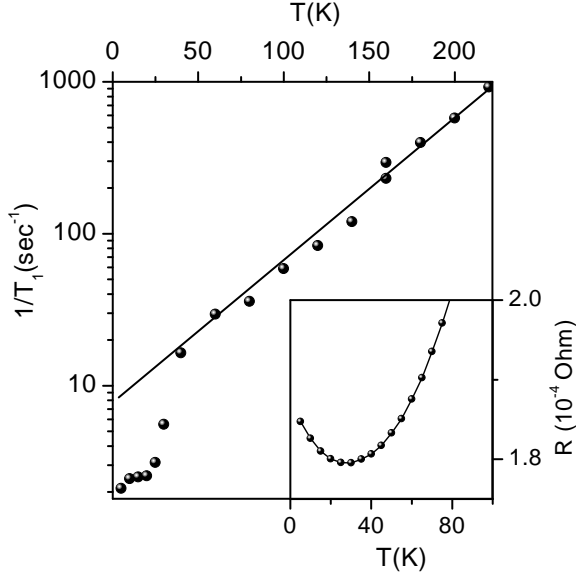


FIG. 2. ^{139}La $1/T_1$ as a function of temperature of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$. The inset exhibits the corresponding R vs. T curve.

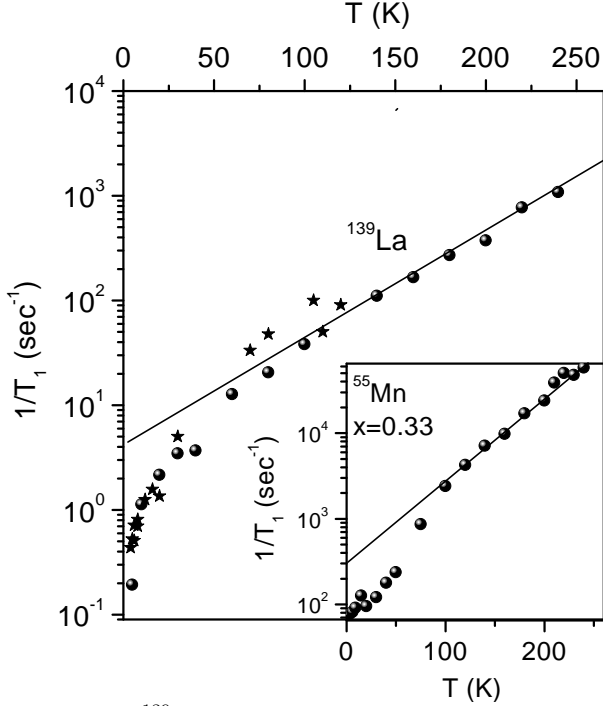


FIG. 3. ^{139}La $1/T_1$ vs. T for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (●) and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (*). The inset exhibits ^{55}Mn $1/T_1$ for $x = 0.33$.

A similar $1/T_1$ behaviour is followed by $x = 0.33$ and 0.5 , as observed in Figure 3. For reasons of comparison, the ^{55}Mn $1/T_1$ vs. T curve for $x = 0.33$, measured at the peak of the FMC signal at $\nu \simeq 375$ MHz [3], is also shown in the inset of Figure 3. In case of $x = 0.33$, the deviation from the high temperature $1/T_1$ vs. T law is realized

below 80K, whereas for $x = 0.5$ a similar behaviour is observed; however, the experimental error of the $1/T_1$ data points above 100K does not allow precise determination of the pertinent temperature, which defines the inflection point. It is worth to notice that for $x = 0.5$ the reduction of $1/T_1$ at low temperatures takes place deep into the antiferromagnetic phase, hence it concerns enhancement of the electron mobility within the FMC islands that persist below T_N [9], [10].

In order to examine whether the temperature dependence of the local electron mobility is associated with modifications of the OO, detailed I vs. H_1 measurements for $x = 0.25$, 0.33 , and 0.5 were performed as a function of temperature (Figure 4). In case of $x = 0.25$ and 0.33 , by decreasing temperature the maximum of the I vs. T curves is clearly observed to shift to lower H_1 fields. Remarkably, the abrupt reduction of $1/T_1$ is accompanied with the appearance of a second maximum in the I vs. H_1 curves at extremely low H_1 values. This is a direct evidence that the low temperature regime of the FMC phase contains at least two distinct FM electron spin configurations, differing in H_A and therefore OO [18]. By increasing x , the low- H_1 maximum remains unshifted, whereas the initial maximum shifts to higher rf power levels. It is also notable that for $x = 0.25$ and 0.5 , the second maximum appears simultaneously with the onset of the mixed phase, i.e. below $\simeq 30\text{K}$ for $x = 0.25$ [3], and $\simeq 140\text{K}$ for $x = 0.5$ [10]. These results corroborate with (i) recent ^{119}Sn Moessbauer measurements in 1% Sn-doped $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, which indicate the appearance of a third FM signal component for $T < 120\text{K}$ [19], and (ii) magnetoresistance experiments in thin films of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [20], which show that below 100K magnetoresistance anisotropy changes rapidly from two-fold to four-fold.

In view of the up-to-now discussion, the following picture may be envisaged: For $x \geq 0.175$ in the low temperature regime of the $T - x$ magnetic phase diagram the system breaks into FMC regions with high conductivity and FMI regions with low conductivity, which differ mainly in the orbital structure. In the FMC regions more than one orbital configurations may be realized, as implied by the subsequent shift of the prime maximum in the I vs. H_1 curves, by varying doping or temperature. This is in conformity with recent theoretical calculations [21], which have shown that by increasing x the FM state is realized, whereas OO may change continuously from orbital G $(x^2 - y^2)/(3z^2 - r^2)$ near $x = 0$, to orbital C $(x^2 - y^2)/(3z^2 - r^2)$ for $x \approx 0.3$, and orbital A $[(3z^2 - r^2) + (x^2 - y^2)]/[(3z^2 - r^2) - (x^2 - y^2)]$ for $0.4 \leq x \leq 0.7$. Remarkably, the calculated energy difference among these states is very small [21], suggesting the presence of strong orbital fluctuations. In such a case, the formation of islands of an orbital liquid with extremely low H_A is possible. This might give an explanation to the appearance of the maximum at extremely low H_1 field in the I vs. H_1 experiments. In this scenario, by increasing temperature the onset of Jahn-Teller distortions [22]

might lift the degeneracy of the various states, and the orbital liquid would freeze in the high temperature FMC orbital configuration.

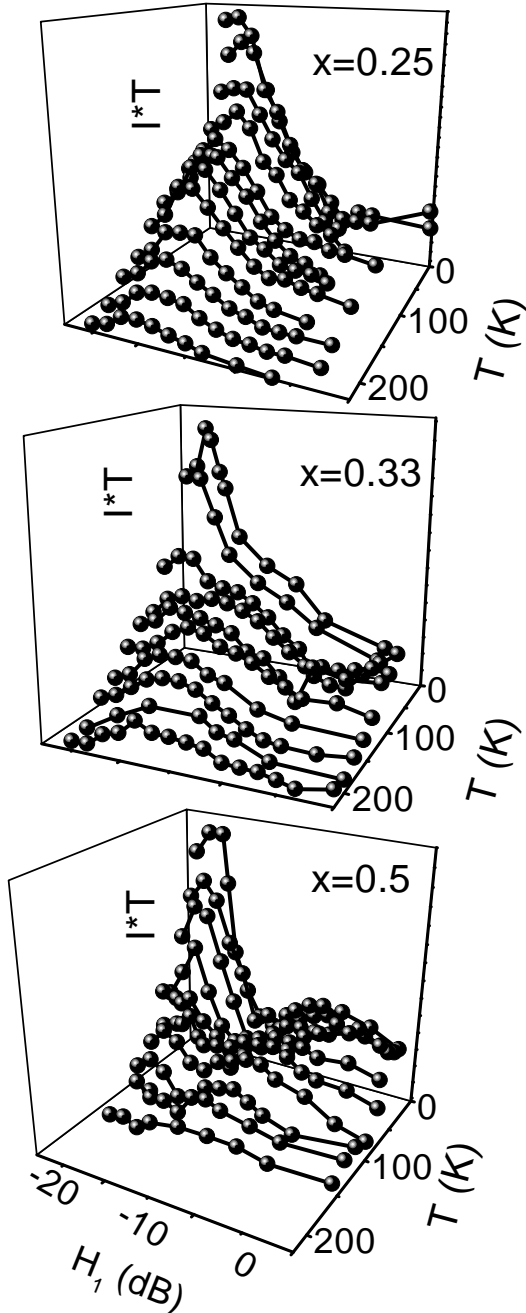


FIG. 4. ^{139}La NMR signal intensity as a function of the rf field H_1 at various temperatures, for $x = 0.25$, 0.33 , and 0.5 .

In conclusion, ^{139}La $1/T_1$ and rf enhancement measurements in La-based manganese perovskites provide clear evidence that differences in OO underly phase segregation tendencies into FM states with high (respectively poor) e_g electron mobility. At low temperatures where the effect of Jahn-Teller distortions is minimized, NMR experiments suggest that degeneracy in the energy of

these states may lead to the appearance of orbital liquid regions, in agreement with recent theoretical predictions [21].

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